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Effect of annealing and UV illumination on properties of nanocrystalline ZnO thin films

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ABSTRACT

ZnO thin films with preferred orientation along the (002) plane were prepared onto the glass substrates by the sol-gel spin coating method for different post- annealing temperatures. The XRD study confirms that the thin films grown by this method have good crystalline hexagonal wurtzite structure. The optical band gap of the samples was determined from UV-visible spectra. It is found that the size of the ZnO grains increase and the optical band gap of the films decrease as the annealing temperature increases from 350°C to 550°C. The transmittance of the film in the visible range was about 75%, 85% and 65% for 350°C, 450°C and 550°C annealed samples respectively. SEM images of the films show worm shaped structures at 350°C and distinct grains in films annealed above 350^0C. Photoluminescence spectral study reveals that all the samples exhibit violet luminescence. The resistivity of the ZnO films found to reduce drastically from mega ohm to ohm range as a result of further vacuum annealing treatment of samples. The variation of electrical resistivity with respect to intensity of UV illumination over the samples has been reported.

Keywords: *Sol-gel method; ZnO thin films; Post annealing; UV-vis; PL; FTIR; XRD; SEM; Resistivity; UV illumination.*

INTRODUCTION

ZnO is a very attractive material for electronic, photovoltaic and optoelectronic applications. It is a wide and direct band gap(~3.37 eV) II-VI semiconductor with many applications such as a transparent conductive contact, solar cell, thin film gas sensor, varistor, luminescent material etc.,[1,2]. In particular ZnO films oriented along the c-axis have been used as surface acoustic wave devices because of the large piezoelectric constant [3, 4].

The grain size of ZnO film can be exploited for improving the performance of various optoelectronic devices. However, the important crystalline properties of ZnO thin films strongly depend on the growth condition, growth techniques and the substrate.

ZnO thin films have been deposited already by various techniques such as spray pyrolysis [5], magnetron sputtering [6], chemical vapour deposition [7], spin coating and dip coating methods [8-10].

Sol-gel processes are particularly adapted to produce colloids and films of ZnO in a simple, low cost and highly controlled way [11, 12]. In this work, ZnO thin films were prepared by sol-gel spin coating technique and the films were post annealed at 350°C, 450°C and 550°C. The dependence of structural, optical and electrical properties on post annealing temperature was studied. The variation in resistivity of the ZnO films on vacuum annealing and on UV illumination is also reported.

EXPERIMENTAL

ZnO thin films were deposited by sol-gel spin coating method onto the glass substrates. Taking Zinc acetate dihydrate as a starting material, 2-methoxyethanol and monoethanolamine (MEA) were used as solvent and stabilizer, respectively. 0.3 M Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature, keeping the molar ratio of MEA to Zinc acetate at 1. Then the solution was stirred at 60°C for 1 hour to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was made one day after the solution was prepared. The coating solution was dropped onto glass substrate, which was rotated at 4000 rpm for 30 s by using the spin coater. As the thermal decomposition temperature of the Zinc acetate is 240°C and the crystallization of the ZnO film begins at about 250°C [13], the film was annealed at 300°C for 10 minute to evaporate the solvent and to remove the organic residuals. The procedure from coating to drying was repeated for six times. The film was then annealed in air at 350°C for 1 hour. Two more samples were also prepared by the same procedure by varying the post annealing temperature as 450°C and 550°C.

Crystallinities of the ZnO thin films were studied by an X'PERT-PRO X-ray diffractometer using the $CuK\alpha_1$ radiation (λ=1.54059Å) in the range of 2θ between 20° and 80°. The surface of the films was observed with Scanning Electron Microscope (SEM). The optical study of these films was carried out at room temperature using Shimadzu UV-Vis 1800 Spectrophotometer in the wavelength range from 200 to 800 nm. FTIR measurements were performed over range 400 cm^{-1} to 5000 cm^{-1} using Shimadzu 8400S Infrared spectrometer. The photoluminescence characteristics of ZnO thin films were evaluated by Perkin Elmer LS55 Spectrofluorometer. Electrical resistivity measurement at room temperature was made by the linear Four-probe method.

RESULTS AND DISCUSSION

Structural Properties

In order to study the vibrational properties of molecules in the synthesized material, the precursor solution is dried to get ZnO powder and FTIR spectral study is done for it. Figure 1 shows the FTIR spectrum of ZnO powder annealed at different temperatures. The FTIR spectrum of the ZnO powder annealed at 350°C shows a peak at 1595 cm^{-1} which represent asymmetric C=O stretching of zinc acetate and another peak at 3485 cm^{-1} which belongs to O-H stretching of hydroxyl group, in addition to two peaks at 474 $cm^{-1}$and 2350 cm^{-1} which are due to Zn-O stretching and CO_2 on the metallic cations respectively [14-16]. The C=O stretching and O-H stretching peaks are found to disappear as the annealing temperature is increased above 350°C, while the Zn-O stretching and CO_2 peaks are found to present in all the three samples.

Figure 2 shows the X-ray diffraction patterns of Zinc oxide films prepared at different annealing temperatures. The obtained peaks in the diffraction pattern confirm the hexagonal wurtzite structure of ZnO. The film deposited on glass at the annealing temperature of 350°C does not have any preferred orientation. However three weak peaks which belong to the (100),(002) and (101) planes of ZnO were observed for this film. The ZnO films

annealed at 450°C and 550°C are highly c-axis oriented showing a prominent (002) peak and less intense (100) and (101) peaks. It indicates that the grains preferably grow along the (002) plane [17]. The grain size D of crystallites was calculated using the Debye Scherrer's formula given by,

$$D = \frac{k\lambda}{\beta \cos\theta} \text{.....(1)}$$

Where, D is the grain size of crystallite, k (=0.9) shape factor for spherical particle, λ (=1.54059Å) is the wavelength of X-ray used, β is the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The sizes of the grains in the films on glass were found to be 3.5 nm, 43.5 nm and 61.5 nm for samples annealed at temperatures 350°C, 450°C and 550°C respectively. It was observed that the grain size increases with increase in annealing temperature [18-20]. The grain size and the corresponding Full Width Half Maximum (FWHM) values of the three samples are shown in Table 1. The increase in intensity of (002) reflection with increase in annealing temperature indicates the enhancement of the ZnO crystallinity with preferred orientation [21]. This result shows that increase of annealing temperature accelerates the migration of atoms to the energy favourable positions [2]. The dislocation density δ, which represents the amount of defects in the film, was determined from the formula ($\delta=1/D^2$)[8]. Dislocation density decreases with increasing annealing temperature [Table1].

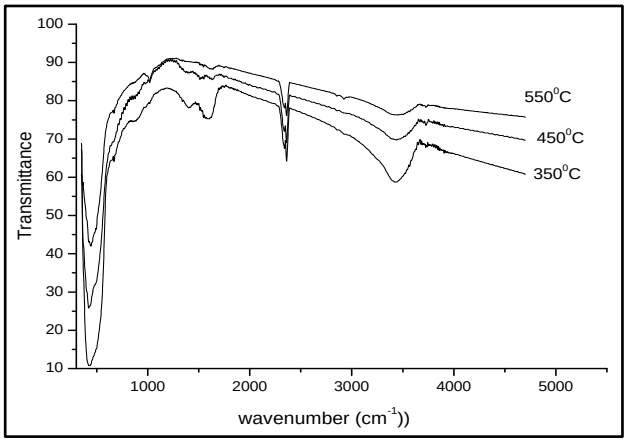

Fig. 1. FTIR spectra of ZnOpowder annealed at different temperatures

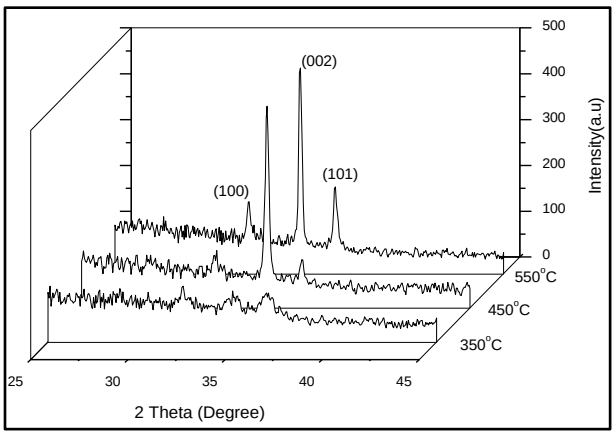

Fig. 2. X-ray diffraction spectra of ZnO thin films for different annealing temperatures350°C , 450°C and 550°C

Table 1. Post annealing effect on Grain size, Strain and Stress

Annealing temperature (°C)	FWHM	Grain size (nm)	Dislocation density δ(nm^{-2})	Strain	Stress (*10^9 pa)
350	2.5112	3.5	0.0816	-0.00242	0.56386
450	0.1996	43.5	0.0005	-0.00341	0.79453
550	0.1412	61.5	0.0003	-0.00325	0.75725

Strain and stress values of the films were calculated by using the values of the lattice spacing obtained from XRD results. The corresponding stress values were calculated using the equation,

$$\sigma = -233\times10^9 \varepsilon^{hkl} \text{.....(2)}$$

where $\varepsilon^{hkl} = \frac{(d^{hkl} - d_0^{hkl})}{d_0^{hkl}}$ is the elastic strain of the (hkl) planes, d_0^{hkl} is the strain free lattice spacing of the (hkl) lattice plane and d^{hkl} is the lattice spacing of the (hkl) plane of the film[22].

The stress and strain values of ZnO thin films are also shown in Table 1. Figure 3 shows the relationship of annealing temperature with grain size and stress. The obtained stress values are positive which confirm the tensile stress and therefore the strain measured for these films are compressive. At low annealing temperatures, there is no enough energy for atoms to move to low energy sites, which induces more strain in the films [2].

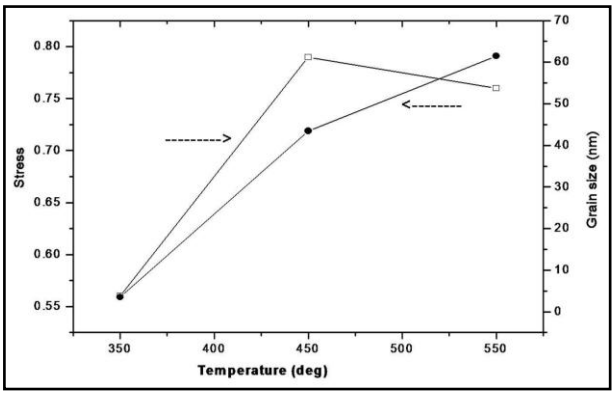

Fig. 3. Relation between grain size, stress and annealing temperature

The lattice constants *a* and *c* were calculated respectively from (100) and (002) peaks by using the well-known formula of analytical method given by,

$$\frac{1}{d_{hkl}^2} = \frac{4\left(h^2+hk+k^2\right)}{3a^2}+\frac{l^2}{c^2} \quad \text{.....(3)}$$

The Zn-O bond length L was calculated by,

$$L = \sqrt{\left(\frac{a^2}{3c^2}+\left(\frac{1}{2}-u\right)^2 c^2\right)} \quad \text{.....(4)}$$

Where the parameter u for wurtizite structure related to *a* and *c*, is given by,

$$u = \frac{a^2}{3c^2} + 0.25 \quad \text{.....(5)}$$

The lattice constant values *a,c* and Zn-O bond lengths are listed in Table 2 and these values are found to coincide well with previous report [8].

Table 2. Post annealing effect on Lattice parameters and Bond length

Annealing temperature (°C)	Lattice Parameter (Å)		Bond length (Å)
	a	c	
350	3.2325	5.1935	1.9689
450	3.2363	5.1882	1.9700
550	3.2389	5.1900	1.9710
JCPDS (36-1451)	3.2490	5.2060	---

Figure 4(a-c) shows the SEM images of the ZnO films. At low annealing temperature (350°C) worm like structures of average width of 0.5µm were observed all over the surface of the thin film (Figure 4a). At 450°C, grains were found to appear and the film annealed at 550°C shows a uniform film with grains of distinct boundaries.

Optical properties

Figure 5 shows the UV-visible transmission spectra of ZnO thin films. The transmittance of the films in the visible range was about 75%, 85% and 65% for samples annealed at 350°C, 450°C and 550°C respectively. The film deposited at 450°C was found to be highly transparent in the visible range. A decrease in transmittance was observed at the higher annealing temperature (550°C) which may be due to more scattering of light in the grain boundaries and increase of surface roughness of the film [17]. This result is in accordance with the findings from XRD data and SEM images, where the XRD data show increase in grain size with annealing temperature and SEM picture reveals distinct grain boundaries at 550°C. A shift in absorption edge towards longer wavelength was observed with increase in annealing temperature.

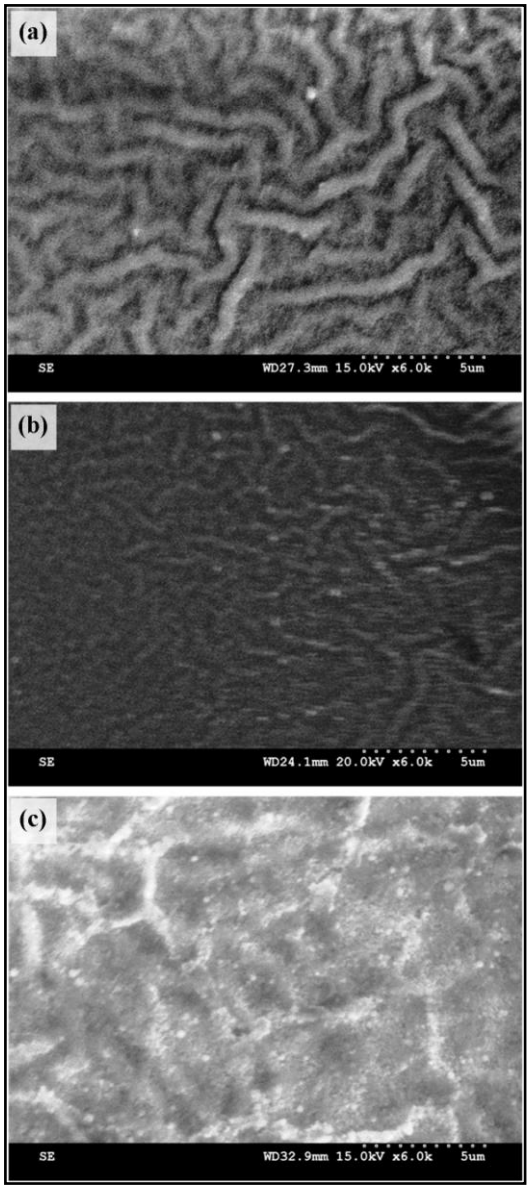

Fig. 4. SEM images ofZnO thin films annealed at (a) 350°C(b) 450°C(c) 550°C

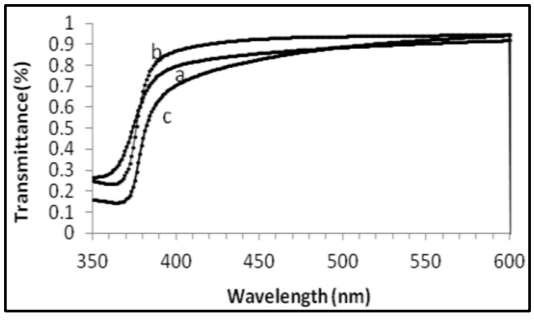

Fig. 5. Transmittance spectra of ZnO thin films

(a)350°C (b)450°C(c)550°C.

The optical band gap of ZnO thin films from UV-visible spectra were estimated using Tauc's relationship given as

$$\alpha h\nu = A\,(h\nu - E_g)^{\frac{1}{2}} \quad \text{.....(6)}$$

Where α is the absorption coefficient, *hν* is the photon energy and *A* is a constant for direct transition. The energy gaps were estimated from the extrapolation of the linear portion of $(\alpha h\nu)^2$ vs$h\nu$ plot to cut the energy axis. Figure 6(a-c) shows the $(\alpha h\nu)^2$ versus photon energy *(hν)* curves of different films. The band gap was found to be 3.26, 3.24 and 3.23 eV for the films annealed at 350°C, 450°C and 550°C respectively. The decrease in band gap may be attributed to the increase of grain size with annealing temperature [23].

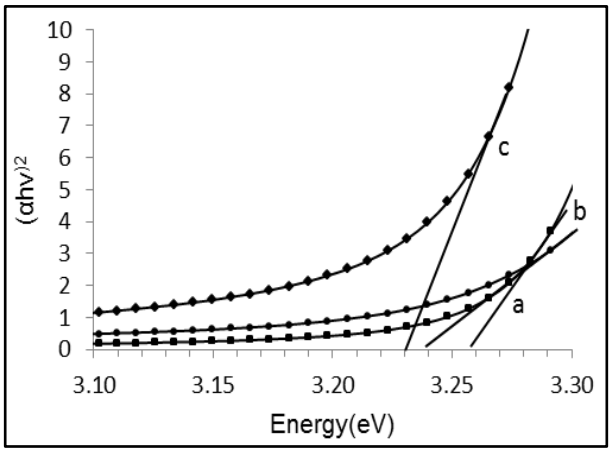

Fig. 6. Plots of $(\alpha h\nu)^2$vs.hν for ZnO thin films annealed at different temperatures a) 350°C (b) 450°C (c) 550°C.

Figure 7 shows the room temperature photoluminescence spectra of the ZnO films deposited at different annealing temperatures. A UV emission peak at about 380 nm was observed in both 450°C and 550°C annealed samples which is absent in 350°C sample. The UV emission peak in photoluminescence is generally due to the free excision emission. The improvement of crystal quality, due to decrease of impurities and structure defects, could result in detectable UV emission at room temperature [24]. The PL spectrum of 350°C annealed sample shows a prominent violet emission peak at 402 nm, where the 450°C and 550°C

samples show the violet emission at 415 nm. The violet luminescence is due to the interface traps existing at the grain boundaries [23]. A large increase in the intensity of violet luminescence peak for 550°C sample may be due to distinct grain boundaries as evident from SEM image and one broad peak at 530 nm (green emission) was additionally found for this sample which may be due to singly ionized oxygen vacancy [25-27].

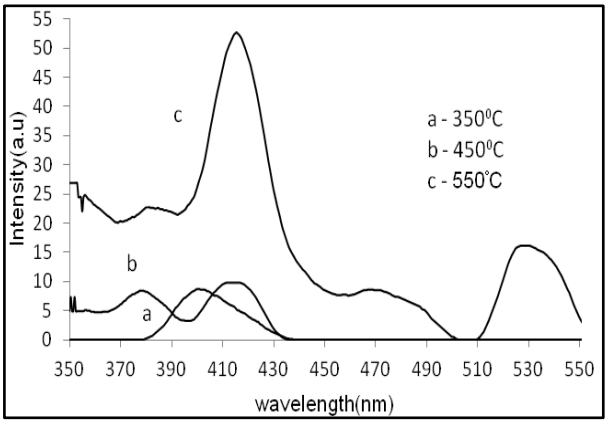

Fig. 7. Photoluminescence spectra of ZnO thin films

Electrical properties

The type of electrical conduction was found to be n-type for these ZnO thin films as verified by the hot-probe technique. Electrical resistivity measurement at room temperature was made by the four-probe method. The I-V characteristic curves for the samples annealed at 450°C and 550°C before and after vacuum annealing are given in Figure 8a and 8b respectively. The electrical resistivities of the samples are found to be at the range of Mega ohm-cm. This high value of resistivity may be due to the chemisorbtion of large number of oxygen molecules at the surface grain boundaries. The adsorbed oxygen will produce potential barrier which hinders the electrical transport [28].In order to reduce the room temperature resistivity of the thin films the samples were vacuum annealed at $4x10^{-5}$ mbar. The resistivity found to fell drastically to ohm-cm range after vacuum annealing for both the samples.

The current at a given voltage for the films under UV-illumination is higher than that under ambient condition. For both the films, the resistivity is found to decrease with UV illumination. The resistivity values are shown in Table 3. As seen from Figure 9a and 9b the photo current increases with increase in intensity of UV light. The variation of resistivity with UV intensity for the two samples is shown in Table 4. The resistivity is found to decrease with increasing UV intensity from 30mW/m^2 to 50mW/m^2. This is due to generation of electrons and holes on exposure to UV light. The formation of defects in ZnO thin films such as doubly ionized Vo^{2+} or singly ionized Vo^{+} oxygen vacancies, may also generates free electrons on UV illumination [29].

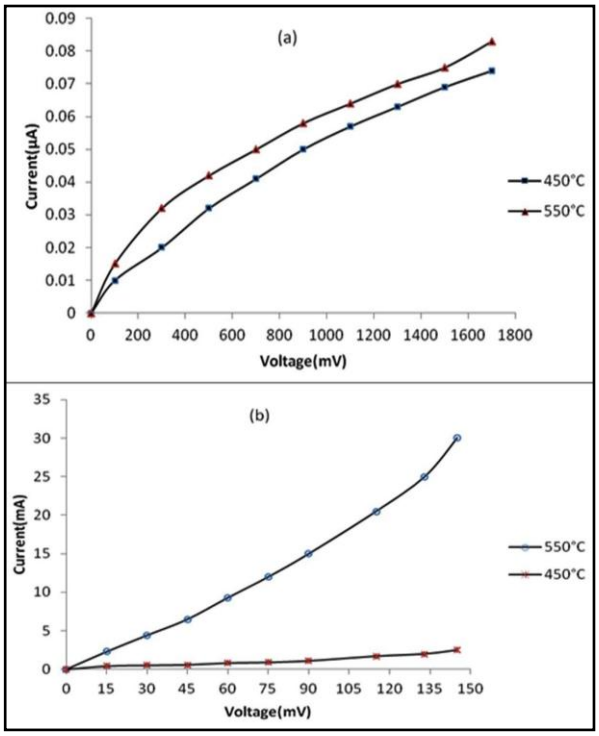

Fig. 8. I-V characteristic curves for thesamples (a) before and (b) after vacuum annealing.

Table 3. Resistivity variation after vacuum annealing and UV illumination

Temperature	R(Ωcm)	$R_{vacuumannealed}$ (Ωcm)	$R_{UV\ illuminated}$ (Ωcm)
450°C	3.8×10^{6}	14.3	0.77

550°C	3.2×10^6	1.3	0.17

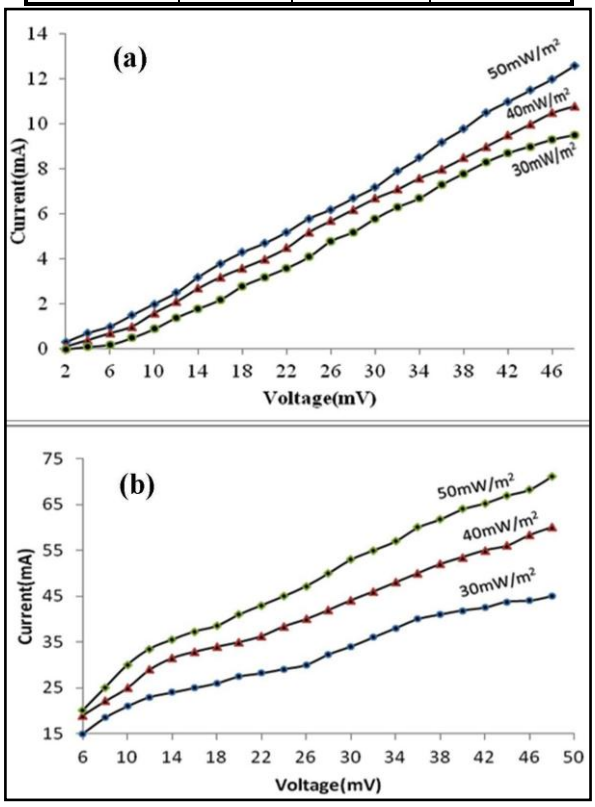

Fig. 9. I-V characteristic curves during various UV illuminations over the samples (a) annealed at 450°C (b) annealed at 550°C.

Table 4. Resistivity variation for various UV illuminations

Flux intensity (mW/m^2)	Resistivity (Ωcm)	
	450°C	550°C
30	1.84	0.17
40	1.09	0.13
50	0.95	0.11

The responsivity R, which is the ratio of the photocurrent to the incident optical power which is given by, $R=I_{ph}/P_{inc,\ where} I_{ph}$ is the photo current and P_{inc} is the incident optical power. The responsivity of ZnO films for the intensity $50mW/m^2$ is plotted in Figure 10. The responsivity of the film for a particular applied voltage is higher for the film annealed at 550°C than for the film annealed at 450°C.

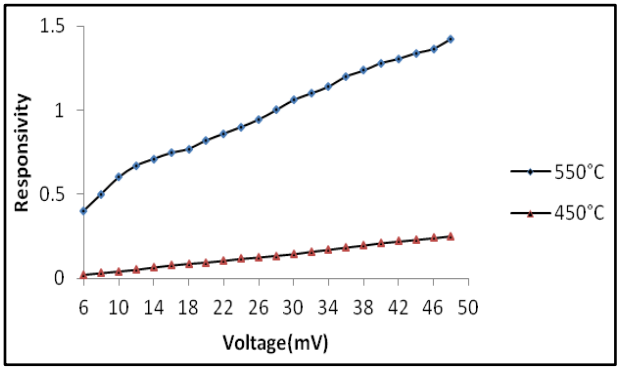

Fig. 10. Responsivity of the films at $50mW/m^2$

CONCLUSIONS

The structural, optical and electrical properties of sol-gel spin coated ZnO thin films for various annealing temperatures have been investigated. The XRD spectra indicate that the films are c-axis oriented films. The grain size of crystallites was found to vary in the range of 3.5 to 61.5 nm and the optical band gap energy in the range of 3.26 to 3.23 eV with variation in annealing temperature from 350°C to 550°C. The annealing temperature found to have influence on the grain size and quality of the films. SEM images also confirm the formation of grains with distinct boundaries at higher annealing temperatures. The PL emission from the films was observed at both UV and visible range at room temperature. The violet photoluminescence of ZnO thin film at room temperature shows a possibility of application to inorganic photoluminescence devices. The electrical study shows that the films have n-type conductivity. The electrical resistivity of the films found to reduce from MΩcm range to Ωcm range after vacuum annealing treatment. The UV illumination over the samples reduced the resistivity further by 10 times. These modifications in the electrical resistivity of ZnO film due to vacuum annealing or UV illumination makes it as a potential candidate for photovoltaic application.

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